Atmospheric Aging of Internally Mixed Sea Salt and Organic Particles: Surprising Reactivity of NaCl with Weak Organic Acids

A. Laskin,[1,*] R. C. Moffet,[2,†] M. K. Gilles,[2] J. D. Fast,[3] R. A. Zaveri,[3] B. Wang,[1] J. Shutthanandan[1]

[1]*William R. Wiley Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, Washington, 99352, USA.*
[2]*Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, 94720, USA.*
[3]*Atmospheric Science and Global Change Division, Pacific Northwest National Laboratory, Richland, Washington, 99352, USA.*
[†]*Currently at Department of Chemistry, University of the Pacific, Stockton, California, 95211, USA*

Chemical imaging analysis of internally mixed sea salt/organic particles collected on board the Department of Energy (DOE) G-1 aircraft during the 2010 Carbonaceous Aerosols and Radiative Effects Study (CARES) was performed using electron microscopy and X-ray spectro-microscopy techniques. Substantial chloride depletion in aged sea salt particles was observed. This depletion could not be explained by the known atmospheric reactivity of sea salt with inorganic nitric and sulfuric acids.

Field evidence is presented showing that chloride components in sea salt particles may effectively react with organic acids releasing HCl gas to the atmosphere, leaving behind particles depleted in chloride and enriched in the corresponding organic salts. While formation of the organic salts products is not thermodynamically favored for bulk aqueous chemistry, these reactions in aerosol are driven by high volatility and irreversible evaporation of the HCl product from drying particles. These field observations were corroborated in a set of laboratory experiments where NaCl particles mixed with organic acids were found to be depleted in chloride. Combined together, the results indicate substantial chemical reactivity of sea salt particles with secondary organics that has been largely overlooked in the atmospheric aerosol chemistry. Atmospheric aging, and in particular hydration-dehydration cycles of mixed sea salt/ organic particles may result in formation of organic salts that will modify the acidity, hygroscopic and optical properties of aged particles.

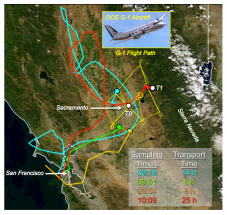
Acid displacement reactions of sea salt chlorides with inorganic acids (present in the atmosphere) result in chloride depletion

$$^{\dagger}NaCl\ (aq)\ +\ HA\ (aq, g)\ \leftrightarrow\ ^{\dagger}NaA\ (aq)\ +\ HCl\ (aq, g)$$

†NaCl denotes chloride salts of sea water, and HA are atmospheric acids such as HNO_3 (nitric acid), H_2SO_4 (sulfuric acid), and CH_3SO_3H (methanesufonic acid, MSA). These reactions release volatile HCl (g) to the atmosphere. The remaining particles are enriched in the corresponding salts and depleted in chloride.

Low volatility carboxylic acids are inherent constituents of SOA formed from both biogenic and anthropogenic precursors. Hence, particles of mixed NaCl/SOA composition may undergo similar reactions processes. These reactions would liberate HCl(g) and promote the formation of organic salts in the particle phase.

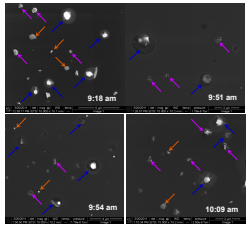
June 15th All Particle Classes



CARES 2010 June 15th G-1 flight path (yellow line)

Colored circles correspond to the collection locations for samples selected for microscopy analysis.

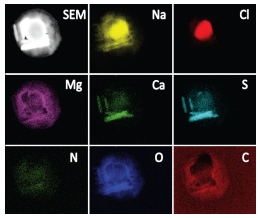
Corresponding blue, green, beige, and red lines indicate the forward trajectories of particles released at the ocean surface, based on a coupled mesoscale & Lagrangian particle dispersion modeling system, that correspond to the time and space location of the collection aboard the G1.



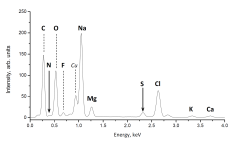
Sea salt particles

Sulfate particles w/ minor sea salt

Sulfates

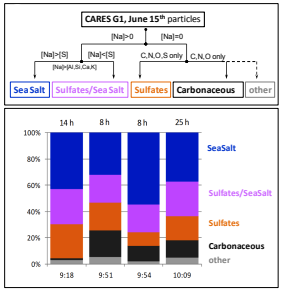


SEM images and EDX elemental maps of a single particle showing characteristic internal heterogeneity of aged sea-salt particles from the CARES field study.



Particle EDX spectrum. The low intensity Cl signals indicate remarkable chloride depletion, while the low intensity of N and S suggest only modest formation of nitrates and sulfates.

The presence of C, Mg, and Na in the halo area is likely due to formation of organic salts.

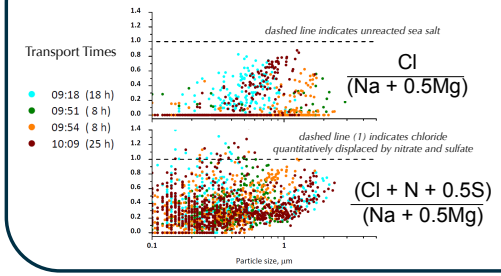


Classification Scheme

Particle Classes
(CCSEM/EDX analysis)

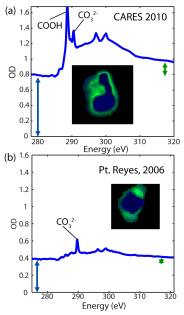
SeaSalt
SeaSalt/Sulfate
Sulfates
Carbonaceous
Other

June 15th Sea Salt Particles CCSEM/EDX Elemental Ratios



Chloride Depletion

Not accounted for by reaction with nitric & sulfuric acids



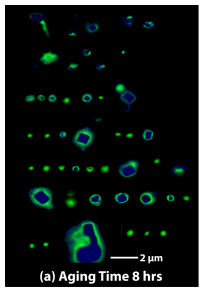
STXM maps and NEXAFS spectra of organic constituents in sea salt particles

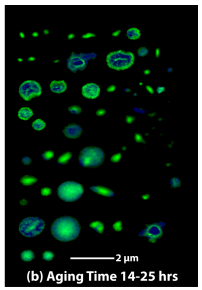
CARES Aged Sea Salt Particles

Organic material has a characteristic peak at 288.5 eV attributed to the presence of carboxylic acids from anthropogenic sources.

Fresh Sea Salt Particles (Pt. Reyes National Seashore)

Note: 290.4 eV peak is attributed to carbonates present in sea water. The carbonates remain unreacted during the aging process and are detected in both fresh and aged particles.





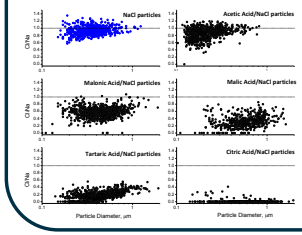
Particle STXM/NEXAFS maps corresponding to different transport times

organic carbon constituents inorganic regions

Changes in morphology, mixing, carbon content & bonding

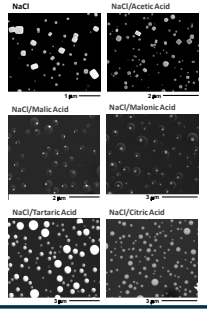
Complementary Laboratory Studies

Cl/Na ratios measured by CCSEM/EDX from dry residues of NaCl, and mixed organic acid/NaCl (1/1 molar ratio) particles.



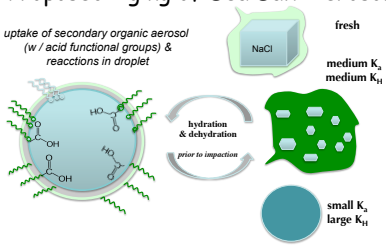
Cl/Na below unity (dashed lines)

indicate Cl depletion by organic acids.



Proposed Aging of Sea Salt Aerosol

uptake of secondary organic aerosol (w / acid functional groups) & reacctions in droplet



$$NaCl\ (aq)\ +\ HA\ (aq, g)\ \leftrightarrow\ NaA\ (aq)\ +\ HCl\ (g)$$

Complex interplay of acid strength, & solubility

Acids	Molecular formula	Molar mass ($g\ mol^{-1}$)	Solubility† in water (g L^{-1} at 20 °C)	Acidity† K_{a1}(aq)	Henry's Law Constant, k_H (M/atm, at 25 °C)
Hydrochloric	HCl	36.46	720	$>1\times10^{7}$	$<2\times10^{1}$
Sulfuric	H_2SO_4	98.08	miscible	$>1\times10^{3}$	$>1\times10^{5}$
Methanesulfonic	CH_3SO_3H	96.11	miscible	7.9×10^{2}	8.2×10^{11}
Nitric	HNO_3	63.01	miscible	$>2\times10^{1}$	$>2\times10^{5}$
Acetic	$C_2H_4O_2$	60.05	miscible	1.8×10^{-5}	$>4.1\times10^{3}$
Malonic	$C_3H_4O_4$	104.06	miscible	1.5×10^{-3}	4.0×10^{6}
Malic	$C_4H_6O_5$	134.09	558	3.9×10^{-4}	2.0×10^{13}
Tartaric	$C_4H_6O_6$	150.09	1330	1.0×10^{-3}	1.0×10^{16}
Citric	$C_6H_8O_7$	192.12	730	8.4×10^{-4}	2.0×10^{19}

Although very little dissociation occurs with a weak acid, if the Henry's law constant is large, as the particle dries the loss of HCl to the gas phase (small Henry's law constant) pushes the reaction towards the products.

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